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(54) Title: COLOURED ANHYDROUS GEL ELEMENT

(57) Abstract: A coloured anhydrous gel element for perfuming or deodorising air or enclosed spaces which element is formed by cross-linking a functionalised liquid polymer selected from maleinised polybutadiene, maleinised polyisoprene or a copolymer of ethylene and maleic anhydride with a cross-linking agent which contains at least one complementary functional group in the presence of an non-aqueous perfume or deodorising base and a least one metal-free solvent dye which is soluble in the non-aqueous perfume or deodorising base, or which is provided as a solution in a non-aqueous solvent which is compatible with the non-aqueous perfume or deodorising base. The gel elements are incorporated into devices which are used as air fresheners or deodorizers.

COLOURED ANHYDROUS GEL ELEMENT

The present invention relates to air care products and, in particular, to products which are capable of diffusing perfume or deodorising components into the surrounding air.

The use of various devices for the diffusion of volatile compounds, for example perfumes deodorising compositions, insect repellents, and the like, into the atmosphere has become increasingly popular in recent years. For example, air-freshening devices or deodorisers are currently used in practically all households to mask bad odours, or to impart fragrances to the ambient air. Various different types of devices are known for the diffusion of volatile compounds into the surroundings. For example, devices of the spray type, such as aerosol sprays, may be used to dispense a liquid composition into the ambient air. Other devices comprise housings enclosing the active ingredients in liquid form. Typically, the diffusion of the active ingredients takes place through membranes permeable to the vapours of said ingredient, or through a wick which is placed in a reservoir containing the ingredients.

Solid state devices are also known which comprise solid materials or carriers impregnated with an active ingredient. Such devices may be formed of various materials which are capable of absorbing the ingredient and subsequently releasing it in a more or less controlled manner. Examples of such known materials include gels, such as agar-agar or sodium stearate gels, synthetic polymer resins, or blocks of mineral material, e.g. plaster or silica.

Solid state devices have the advantage that they are easy to handle and can be easily shaped. Typically, the solid state devices are enclosed within a housing with one or more grills which communicate with the surrounding air.

The main disadvantage with solid state devices is that the release of active ingredients from the blocks is not constant with time and drops dramatically over the lifetime of the device. Furthermore, such devices are inefficient in that the device may cease to diffuse the active ingredient into the surrounding atmosphere when the outside of the block is spent, even though considerable amounts of the active ingredient may still reside within the core of the block. The residual active ingredient, such as perfume, is thus totally lost.

WO 96/05870 discloses a device for perfuming, deodorising or sanitising air or enclosed spaces which comprises an anhydrous gel element. Such a device is capable of diffusing volatile substances at a relatively constant rate throughout the entire lifetime of the device and, furthermore, is capable of releasing substantially all of the volatile substance into the air or enclosed space within its effective lifetime.

The devices of WO 96/05870, although practically very useful, are unattractive since they are in the form of substantially colourless gels. However, because of the manner in which the gels are formed we found that it was difficult to incorporate dyes or colourants into the gels. Many dyes would not disperse within the system and resulted in unattractive non-homogenous products in which the dye was not uniformly dispersed therethrough. Neither the colourless gels of WO 96/05870, nor the non-homogenous coloured gels would be attractive to the purchaser of such devices which generally will be on

display in the room or space which they are intended to perfume or deodorise.

We have now found that homogenous, coloured anhydrous gels can be prepared from the components as disclosed in WO 96/05870 if a very careful selection is made of the dyes for incorporation therein. The present invention is predicated upon this finding.

Accordingly, the present invention provides a coloured anhydrous gel element for perfuming or deodorising air or enclosed spaces which gel element is formed by cross-linking a functionalised liquid polymer selected from maleinised polybutadiene, maleinised polyisoprene or a copolymer of ethylene and maleic anhydride with a cross-linking agent which contains at least one complementary functional group in the presence of a non-aqueous perfume or deodorising base and at least one metal-free solvent dye which is soluble in the non-aqueous perfume or deodorising base or which is provided as a solution in a non-aqueous solvent which is compatible which the non-aqueous perfume or deodorising base.

The present invention also provides a process for preparing a coloured gel element as defined above which comprises cross-linking the functionalised liquid polymer with the cross-linking agent in the presence of the non-aqueous perfume or deodorising base and at least one metal-free solvent dye.

By the term "functionalised liquid polymer" as used herein is meant a material which is liquid at room temperature and which has a viscosity of not more than 5 PaS at 25°C, preferably from 0.25 to 1.0 Pas.

The functionalised liquid polymer which is used in the present invention is preferably a maleinised polybutadiene having a number average molecular weight of from 5,000 to 25,000 or a maleinised polyisoprene having a number average molecular weight of from 200,000 to 500,000. Examples of these materials are given in EP-A-0023084. These materials are commercially available and are sold under the trade name LITHENE (Revertex Limited). Amongst the different grades of LITHENE which are available particularly good results have been obtained using LITHENE N4-9000-10MA where 9000 represents the molecular weight of the polybutadiene before maleinisation and 10MA indicates the degree of maleinisation in this case 10 parts of maleic anhydride per 100 parts of polybutadiene (i.e. about 9.1%). LITHENE N4-B-10MA and LITHENE N4-5000-10MA are also particularly useful.

Alternatively, the liquid polymer may comprise a copolymer of ethylene and maleic anhydride, for example.

Examples of cross-linking agents which may be used in forming the anhydrous gels are as follows:

- alkylpropyldiamines having an ethoxylated or propoxylated higher aliphatic chain such as the products sold under the trade name DICRODAMET (Croda Chemicals Limited);

- ethoxylated or propoxylated primary fatty amines sold under the trade name CRODAMET, for example CRODAMET 02 (oleylamine having 2 ethylene oxide units per molecule);

- polyoxyalkylenediamines such as those sold under the trade name JEFFAMINE (Huntsman Corporation) in particular the D and ED series,

for example JEFFAMINE D-400, JEFFAMINE EDR-148 and Jeffamine D-2000;

- polyoxyalkylenetriamines such as those sold under the trade name JEFFAMINE (Huntsman Corporation) in particular the T series, for example JEFFAMINE T-403.

It is also possible to use as the cross-linking agent polybutadiene having a hydroxylic functionality known as HPPB (Revertex Limited) which gellifies when admixed with maleinised polybutadiene. Sometimes the use of specific catalysts allow a better control of the gel formation and examples of such catalysts are the tertiary amines (e.g. DAMA 1010; origin: Albermarle SA). Mixtures of Hycar CTBN 1300 x 21 which is an amine terminated liquid polybutadiene/acrylonitrile copolymer (origin: B.F. Goodrich) and maleinised polybutadiene are particularly advantageous.

The functionalised liquid polymer and the cross-linking agent are mixed in a molar ratio of between 3:1 and 5:1 preferably of about 1:1, based on the molar ratio of the functional groups which are present.

The perfume base which is used in the device of the invention may comprise any of the current bases used in perfumery. These can be discrete chemicals; more often, however, they are more or less complex mixtures of volatile liquid ingredients of natural or synthetic origin. The nature of these ingredients can be found in specialised books of perfumery, e.g. in S. Arctander Perfume and Flavor Chemicals, Montclair N.J., USA 1969) or Perfumery, Wiley-Intersciences, New York, USA 1994.

The perfume base may be replaced by a deodorising base, such as a base which comprises a deodorising composition.

The characteristic feature of all the compositions of the present invention is that the liquid polymer, cross-linking agent and dye which are used in the preparation of the gellified composition are all soluble in the perfume or deodorising base. Optionally, one or more of the liquid polymer, cross-linking agent or dye may be dissolved in a solvent which is compatible with the perfume of deodorising base, but generally this is not necessary since the components will dissolve in the active base.

The perfume or deodorising base is non-aqueous and will generally constitute from 50 to 95% by weight, preferably from 60 to 90% by weight, more preferably from 70 to 85% by weight of the gel element.

Optional additives which may be included in the gel composition include plasticisers such as diethylphthalate.

Examples of suitable classes of dyes which may be used in the present invention are monoazo dyes, diazo dyes, anthraquinone dyes or methine dye, provided that the dyes are metal-free solvent dyes. Specific examples of dyes which may be successfully used in the present invention are:

Chemical Characterization	Trade Names
C.I. Solvent Red 27	Fat Red 5B-02 (Clariant)
C.I. Solvent Red 111	Sandoplast Red PFS (Clariant)
C.I. Solvent Yellow 14	Fat Orange R-01

	(Clariant)
C.I. Solvent Yellow 93	Sandoplast Yellow 3G (Clariant)
C.I. Solvent Violet 13	Iragon Violet SV113 (Ciba)
C.I. Solvent Violet 37	Sandoplast Violet FBLP (Clariant)
C.I. Solvent Green 3	Iragon Green SGR3 (Ciba)
C.I. Solvent Green 28	Sandoplast Green G (Clariant)
C.I. Solvent Blue 104	Sandoplast Blue 2B (Clariant)

Dyes such as those listed above are generally in powder form. Accordingly, in order to be useful in the present invention the dye is generally soluble in the perfume or deodorising base. However, it may be possible to use some dyes which are either not soluble in or insufficiently soluble in the said base by using the dyes as concentrated solutions in a non-aqueous solvent which is compatible with the base.

Generally a relatively small amount of dye will be sufficient to colour the anhydrous gel, for example amounts of from 0.01 to 1.0% by weight, typically about 0.05% by weight based on the gel element, may be used.

Many dyes cannot be used in the present invention. Examples of such dyes which either are not metal-free solvent dyes and/or are not soluble in the perfume or deodorising base, are given below:

Chemical Characterization	**Trade Names**
C.I. Solvent Orange 63	Hostalsol Red GG (Clariant)
C.I. Solvent Red 179	Sandoplast Red 2GP

	(Clariant)
C.I. Solvent Red 89	Savinyl Fire Red GLSP (Clariant)
C.I. Solvent Red 91	Savinyl Red 3BLS P (Clariant)
C.I. Solvent Red 127	Savinyl Pink 6BLS P (Clariant)

The anhydrous gel element of the present invention may be used as the active element of a solid state air freshening or deodorising device with the gel element being incorporated within a housing with one or more grilles which communicate with the ambient air.

Alternatively, the gel element may be formed in situ within the recesses or grooves of a solid casing or housing. This type of device does not require the use of a grille to cover the gel element. The recesses or grooves of the solid casing or housing are filled with the mixture of functionalised liquid polymer, cross-linking agent, perfume or deodorising base and dye and the cross-linking reaction to form the gel takes place *in situ*. The gel so-formed thus adheres to the sides and/or bottom of the recesses or groove in order to provide an integral structure.

The present invention will be further described with reference to the following Examples.

EXAMPLE 1

To a vessel containing 63.975g of a perfume base (Lavandair 150.120D; origin - Firmenich SA, Geneva, Switzerland) was added 0.025g of dye (Iragon Violet SVI13; origin -Ciba Speciality Chemicals, Switzerland) with stirring. 17.0g of Lithene N4-B-10MA was then added manually and mixed. In another vessel 16.0g of the

perfume base (Lavender 150.120D) and 3.0g of Jeffamine D-400 were mixed and then added to the original vessel with stirring. After about 5 minutes at room temperature, a purple gel resulted encapsulating the perfume base. Gel setting was complete in about 20 minutes.

EXAMPLE 2

To a vessel containing 63.91g of perfume base (Solar Splash 150.555; origin - Firmenich SA, Geneva, Switzerland) was added 0.09g of dye (Sanoplast Yellow 3G; origin - Clariant UK Ltd, United Kingdom) with stirring. 17.0g of Lithene N4-B-10MA was then added manually and mixed. In another vessel 16.0g of the perfume base (Solar Splash 150.555), 1.12g of Jeffamine EDR-148 and 1.88 g of diethyl phthalate were mixed and then added to the original vessel with stirring. After about 5 minutes at room temperature, a yellow gel resulted encapsulating the perfume base. Gel setting was complete in about 20 minutes.

EXAMPLE 3

To a vessel containing 63.97g of a perfume base (Summer Fruits 150.535; origin - Firmenich SA, Geneva, Switzerland) was added 0.03g of dye (Fat Red 5B02; origin - Clariant UK Ltd, United Kingdom) with stirring. 17.0g of Lithene N4-B-10MA was then added manually and mixed. In another vessel 16.0g of the perfume base (Summer Fruits 15.535), 2.40g of Jeffamine D-400, 0.22g of Jeffamine EDR0148 and 0.38g of diethyl phthalate were mixed and then added to the original vessel with stirring. After about 5 minutes at room temperature, a deep red gel resulted encapsulating the perfume base. Gel setting was complete in about 20 minutes.

EXAMPLE 4

To a vessel containing 63.98g of a perfume base (Nile Blossom 438.910; origin - Firmenich SA, Geneva, Switzerland) was added 0.02g of dye (Iragon Green; origin - Ciba Speciality Chemicals, Switzerland) with stirring. 17.0g of Lithene N4-B-10MA was then added manually and mixed. In another vessel 16.0g of the perfume base (Nile Blossom 438.910), 2.40g of Jeffamine D-400, 0.22g of Jeffamine EDR-148 and 0.38g of diethyl phthalate were mixed and then added to the original vessel with stirring. After about 5 minutes at room temperature, a blue/green gel resulted encapsulating the perfume base. Gel setting was complete in about 20 minutes.

EXAMPLE 5

To a vessel containing 63.97 of a perfume base (Summer Fruits 150.535; origin - Firmenich SA, Geneva, Switzerland) was added 0.03g of dye (Savinyl Fire Red GLSP; origin - Clariant UK Ltd, United Kingdom) with stirring. 170g of Lithene N4-B-10MA was then added manually and mixed. In another vessel 16.0g of the perfume based Summer Fruits 150.535), 240g of Jeffamine D-400, 0.22g of Jeffamine EDR-148 and 0.38g of diethyl phthalate were mixed and then added to the original vessel with stirring. After about 5 minutes at room temperature, a gel resulted, but the colour was not homogeneously distributed throughout resulting in an unattractive aspect. Gel setting was complete in about 20 minutes.

EXAMPLE 6

To a vessel containing 3.998g of a perfume base (Lavandair 150.120D; origin - Firmenich SA, Geneva, Switzerland) was added 0.00156g of dye (Iragon Violet

SVI13; origin - Ciba Speciality Chemicals, Switzerland) with stirring. 1.0625g of Lithene N4-B-10MA was then added manually and mixed. In another vessel 1.0g of the perfume base (Lavandair 150.120D) and 0.1875g of Jeffamine D-400 were mixed and then added to the original vessel with stirring. Once a homogeneous mix was attained, the mixture was added to a suitable decorative device containing grooves which the liquid mix could run through. After about 5 minutes at room temperature, a purple gel, in the shape of the device, resulted encapsulating the perfume base. Gel setting was complete in about 20 minutes.

CLAIMS:

1. A coloured anhydrous gel element for perfuming or deodorising air or enclosed spaces which element is formed by cross-linking a functionalised liquid polymer selected from maleinised polybutadiene, maleinised polyisoprene or a copolymer of ethylene and maleic anhydride with a cross-linking agent which contains at least one complementary functional group in the presence of a non-aqueous perfume or deodorising base and at least one metal-free solvent dye which is soluble in the non-aqueous perfume or deodorising base, or which is provided as a solution in a non-aqueous solvent which is compatible with the non-aqueous perfume or deodorising base.

2. A coloured anhydrous gel element as claimed in claim 1 wherein the dye is C.I. Solvent Red 27, C.I. Solvent Red 111, C.I. Solvent Yellow 14, C.I. Solvent Yellow 93, C.I. Solvent Violet 13, C.I. Solvent Violet 37, C.I. Solvent Green 3, C.I. Solvent Green 28 or C.I. Solvent Blue 104.

3. A coloured anhydrous gel element as claimed in claim 1 or claim 2 wherein the dye constitutes from 0.01 to 1.0% by weight of the gel element.

4. A coloured anhydrous gel element as claimed in any one of the preceding claims wherein the perfume or deodorising base constitutes from 60 to 95% by weight of the gel element.

5. A coloured anhydrous gel element as claimed in claim 4 wherein the perfume or deodorising base constitutes from 70 to 80% by weight of the gel element.

6. A coloured anhydrous gel element as claimed in any one of the preceding claims wherein the functionalised liquid polymer is a maleinised polybutadiene having a number average molecular weight in the range of from 5,000 to 20,000, or a maleinised polyisoprene having a number average molecular weight of from 200,000 to 500,000.

7. A coloured anhydrous gel element as claimed in any one of the preceding claims wherein the cross-linking agent is an alkylpropylamine, an ethoxylated or propoxylated primary fatty amine, a polyoxyalkylenediamine or a polyoxyalkylene triamine.

8. A coloured anhydrous gel element as claimed in any one of the preceding claims wherein the liquid polymer and cross-linking agent are soluble in the perfume, deodorising or sanitising base.

9. A device which incorporates therein a coloured anhydrous gel element as claimed in any one of the preceding claims.

10. A coloured gel element as claimed in any one of claims 1 to 8, or a device as claimed in claim 9, which is an air freshener.

11. A coloured gel element as claimed in any one of claims 1 to 8, or a device as claimed in claim 9, which is a deodorizer.

12. A process for preparing a coloured gel element as defined in any one of claims 1 to 8, 10 or 11 which comprises cross-linking the functionalised liquid polymer with the cross-linking agent in the presence of the non-aqueous perfume or deodorising base and at least one metal-free solvent dye.

13. A process for preparing a device as defined in claim 9 which comprises preparing the colour anhydrous gel element in the device by a process as defined in claim 12.